Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 84 (2014) 940 – 947

Procedia Engineering

www.elsevier.com/locate/procedia

"2014ISSST", 2014 International Symposium on Safety Science and Technology

Dwarf-castor oil made into a suitable biodiesel

Shu-Yao TSAI, Wei-Siou TSENG, Cheng-Tsung WU,Chun-Ping LIN*

Department of Health and Nutrition Biotechnology, Asia University,500, Lioufeng Rd., Wufeng, Taichung41354, Taiwan, China & Department of Medical Research, China Medical University Hospital, China Medical University, 91, Hsueh-Shih Rd., Taichung 40402, Taiwan, China

Abstract

The dwarf-castor could be drought tolerant, pest-resistant, require less artificial care, and biomass oil could be harvested for three times in a year. Differential scanning calorimetry (DSC) will be used to obtain the crystallization temperature and the enthalpy of endothermic and exothermic of the dwarf-castor oil, the biodiesel, petrodiesel, and the environmentally-friendly diesel. Moreover, the infrared spectrometer (FT-IR) will be also used in the results of transesterification for identifying the characteristic functional groups. Furthermore, the heat of combustion and the kinematic viscosity of environmentally-friendly diesel were conducted by bomb calorimeter and viscometer, respectively, which were compared with the various proportion of biodiesel for mixing with petrodiesel, and then to obtain the best condition of mixtures B20 as a suitable environmentally-friendly diesel of dwarf-castor's biodiesel.

Peer-review under responsibility of scientific committee of Beijing Institute of Technology

Keywords: Dwarf-castor; biomass oil; Environmentally friendly diesel; Functional group; Heat of combustion; Kinematic viscosity

1. Introduction

The dwarf-castor growth height is ca. 1.2 meters; it is drought tolerant, pest-resistant, requires less artificial care, and biomass oil can be harvested three times in a year. To date, the dwarf castor is only for harvesting terrestrial biomass by mechanical harvesting in the world. Dwarf -castor has rich oil production, the oil of which is generally refined for making into lubricants, motor oil, and brake oil. Specifically, the castor planted is in tropical regions, the oil-producing reaches approximately 50 % (w/w) [1–3]. It is advantageous for mitigating the risk of a petroleum

* Corresponding author. +886 4 2332 3456 ext1802; fax: +886 4 2332 1126.
E-mail address: cp.lin@asia.edu.tw; chunping927@gmail.com (C.-P. Lin)

Peer-review under responsibility of scientific committee of Beijing Institute of Technology
doi:10.1016/j.proeng.2014.10.519

crisis, to find an appropriate alternative energy or green energy. Actually, not all are suitable for bio-oil as alternative energy and green energy. It is a critical point for biodiesel. First, it does not take food or feed cultivated farmland. Second, large-scale biomass oil must be produced. Dwarf-castor is consistent with the two important lines. Therefore, the dwarf-castor can produce a large amount of biomass oil, which also can improve air quality and inhibit global warming.

The main stages of the dwarf-castor biodiesel production process are as follows: (a) saponification fixes the 12-hydroxy-9-octadecenoic acid, which is used for enhancing the yield of the transesterification reaction and removing impurities, glycerol, and free fatty acid; (b) reduction reaction, which reverts the fatty acids for convenient converting to biodiesel; and (c) acid-catalyzed reaction, which makes thericinoleic acid and methane for fully transesterifying into the fatty acid methyl ester [4–11].

Differential scanning calorimetry (DSC)will be used to obtain the melting temperature, the crystallization temperature, and the enthalpy of endothermic and exothermic of the dwarf-castor oil, the biodiesel, and the environmentally-friendly diesel [12–18].An infrared spectrometer (FT-IR) will be also used in the transesterification for identifying the characteristic functional groups [19, 20].

Good environmentally-friendly diesel has suitable heat of combustion and kinematic viscosity. It is an important performance indicator of biodiesel for mixing with petrodiesel, which is concerned with effective fuel for diesel engine [20, 21]. Here, the heat of combustion and the kinematic viscosity of environmentally-friendly diesel were tested by bomb calorimeter and viscometer, respectively, which were compared the various proportion of biodiesel for mixing with petrodiesel; then, the best condition of mixtures was obtained as a good environmentally-friendly diesel of dwarf-castor's biodiesel [3,22]. It is an important project for developing high quality environmentally-friendly diesel from the dwarf-castor oil.

2. Materials and methods

2.1. Samples

Dwarf-castor beans, which were purchased from castor farmland in Taiwan, were sun dried for five days and then stored a cool and dry environment. The fatty acid profile of dwarf-castor oil is displayed in Fig. 1.

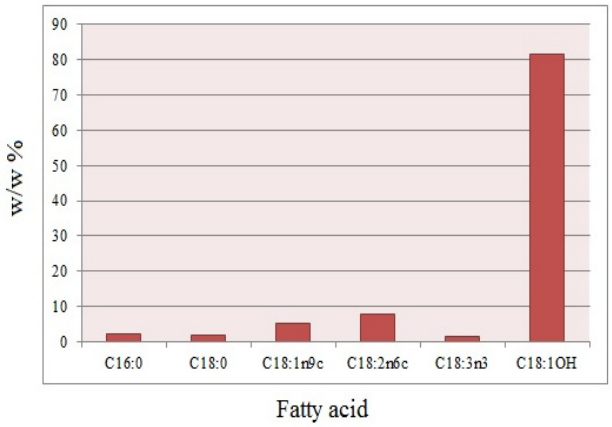

Fig. 1. Dwarf-castor oil major fatty acid profile.

2.2. Transesterification

First, the goal was of fixed fatty acid composition, which was saponified with the three equivalents of sodium hydroxide under ca. 90 °C for three hours, and then the impurities, the free fatty acids, and glycerol were removed to

form the dwarf-castor oil soap. The dwarf-castor oil soap was included in the further transesterification. From the above-mentioned via saponification, which excluded the impurities, the free fatty acids, and glycerol, we could then obtain high purity fatty acid for the next step of the reduction reaction. Second, the reduction reaction was mixed with sulfuric acid to form fatty acids under 85 °C for three hours. Finally, the acid-catalyzed reactions were mixed with dil. sulfuric acid (less than 0.02 % ratio of fatty acid) and methanol (fatty acids: methanol = 1:5) under reflux for overnight.

2.3. Infrared spectroscopy analysis

The fatty acids of dwarf-castor oil and the fatty acid methyl esters of dwarf-castor biodiesel were accreted drop wise onto a KBr disc from a concentrated dichloromethane solution, respectively [19, 20]. Evaporation of the solvent resulted in a uniform film. Infrared spectra were obtained using a Bruker Alpha FT-IR spectrometer. Spectra were assembled in the transmission mode with an unpolarized light beam, at a resolution of 4 cm^{-1} with six scans, and a spectral range of 4000–400 cm^{-1}.

2.4. Differential scanning calorimetry (DSC) tests

Temperature–programmed screening experiments were performed with DSC (TA Q20-RCS90). For DSC analysis on the samples sealed in 20μL aluminum pans, the lid is pressed onto the crucible using the pressure of a heavy mechanic force, and the seal tightens the crucible; the test cell is then sealed manually by a special tool supplied by a special tool equipped with TA's DSC. ASTM E698 was used to obtain thermal curves and the parameters were analyzed. About 1.7 to 2.5mg of the sample was used for obtaining the experimental data. Non-isothermal tests of the scanning rate selected for the programmed temperature ramp were 4, 6, and 8 °C/min for the range of temperature rise chosen from 30–65°C and then cooling down to –30 °C for each endothermic and exothermic reaction experiment, and from 30–300 °C for each thermal stability and phase behavior experiment, respectively.

Comparisons were made of thermal stability and phase behavior experiment of the commercial diesel, the commercial environmentally-friendly diesel, and the various proportion of biodiesel for mixing with petro diesel only, with the programmed temperature ramp of 4 °C/min for the range of temperature rise chosen from 30–65 °C and then cooling down to –30 °C for each endothermic and exothermic reaction experiment and from 30–300 °C. In all studies with DSC thermal analysis, high purity nitrogen was the purge gas and the flow rate was 50 mL/min.

2.5. Kinematic viscosity measurement

Kinematic viscosity measurement is important for diesel engine fuel. It is also an important indicator for biodiesel. To charge the sample into the viscometer, we placed the viscometer into the holder for fixing, and inserted it into the constant temperature bath. A viscometer holder which fits the Cannon-Fenske Opaque viscometer and the Cannon-Manning Semi-Micro viscometer will also fit Cannon-Fenske Routine viscometer. We aligned the viscometer vertically in the bath by means of a small plumb bob in tube. Approximately 10 minutes was allowed for the sample to come to the bath temperature at 40 °C. To measure the efflux time and check run we repeated three times for each sample. We also compared with a commercial diesel and a commercial environmentally-friendly diesel, and the various proportion of biodiesel for mixing with petrodiesel.

2.6. Heat of combustion measurement by bomb calorimeter

Heat of combustion analysis of the samples was conducted on a Parr 1341 oxygen bomb calorimeter instrument. This study conducted a heat of combustion analysis for all samples as follows: (a) To prepare, the water temperature should be approximately 1.5°C below room temperature, for which it is not necessary to use exactly 2000 g, but the amount selected must be duplicated within ± 0.5 g for each experiment. We opened the filling connection control

valve slowly and watched the gage as the bomb pressure rose to the desired filling pressure (usually 30 atm., but never more than 40 atm.); then we closed the control valve. (b) Instead of weighing the bucket it can be filled from an automatic pipet or from any other volumetric device if the repeatability of the filling system is within +/-0.5 mL and the water temperature is held within a 1 ºC range. (C) We let the stirrer run for 5 minutes to reach equilibrium before starting a measured run. Approximately 0.5 g of the all samples was used for acquiring the experimental data. At the end of this period we recorded the time on the timer of Parr 6775 Digital Thermometer and read the temperature.

3. Results and discussion

3.1. Transesterification

From the sequences of saponification, reduction reaction and acid-catalyzed reactions which were conducted for the full process of transesterification, excluding the impurities, the free fatty acids, and glycerol, we successfully obtained the dwarf-castor biodiesel. From Fig. 2, we observed the hydroxyl (–OH) groups of long carbon chain of carboxylic acid, the stretching-vibration absorption peak wave numbers were 3600–3100 cm^{-1}& 2700–2400 cm^{-1} and the stretching-vibration absorption peak wave numbers were 1020 cm^{-1}&850 cm^{-1}, for which the characteristic functional group of 12-hydroxy-9-octadecenoic acid was clearly exhibited in the IR spectrum. In addition, the carbonyl group (–C=O) of carboxylic acids, the stretching-vibration absorption peak wave number was 1760 cm^{-1} and the C–O stretching-vibration absorption peak wave number was 1390–1190 cm^{-1},respectively, which were also obviously showed in the spectrogram.

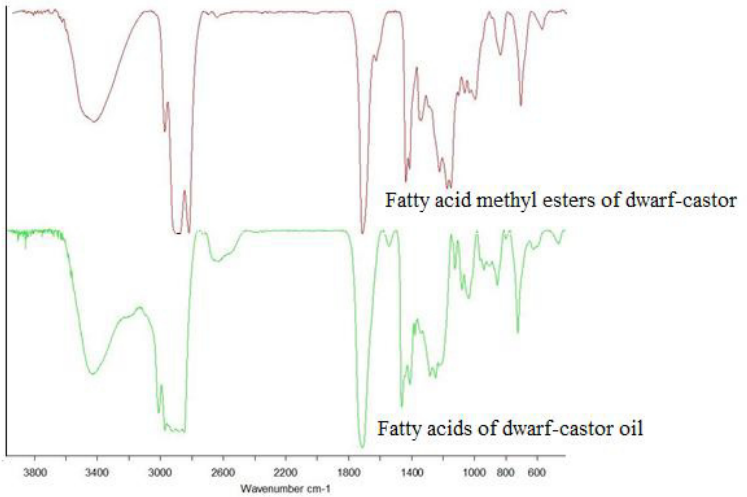

Fig. 2. FT-IR spectrogram of the fatty acids of dwarf-castor oil and the fatty acid methyl esters of dwarf-castor biodiesel.

Fig. 2 shows the hydroxyl (–OH) groups in carboxylic acids could generate methyl groups (–O–CH_3) through methyl transesterification. When the hydroxyl group in carboxylic acids was gradually transesterified, the broad of stretching-vibration absorption peak (3600–3100 cm^{-1}& 2700–2400 cm^{-1}) gradually sharpened, along with the hydroxyl (–O–H)stretching-vibration absorption peak wave numbers 1020 cm^{-1}&850 cm^{-1} and the C–O–H bending-vibration absorption peak wave numbers 1490–1395 cm^{-1} were gradually sharpened too. In addition, from Fig. 2 the hydrogen bond stretching-vibration of intermolecular absorption peak wave number 3350 cm^{-1} and the same plane of O–H bending-vibration absorption peak wave number 1350 cm^{-1} were very clear, which proved the 12-hydroxy-9-octadecenoic acid methyl esters presence. The above transesterified results of fatty acid via FT-IR spectrogram corroborated the accuracy of the transesterification, which proved the dwarf-castor oil formed the biodiesel.

3.2. DSC analysis

The phase behavior of castor oil and castor biodiesel has been characterized by DSC in terms of the temperature and the enthalpy of the phase transition. From Figs. 3–5, the DSC thermograms show the distinct phase transitions, respectively. Three conditions of the onset temperature, the peak maximum temperature, and the endothermic and exothermic reaction of enthalpy associated with the DSC transition, were found for the thermal characteristics of the castor oil and castor biodiesel. In fact, the DSC peak maximum temperature and enthalpy measured for the castor oil and castor biodiesel clearly discriminate the differences. Figs. 3 and 4 show that the DSC thermogram programmed temperature ramp was 4, 6, and 8 °C min^{-1} for the range of temperature rise chosen from 30–65 °C and then cooled to –30 °C for each castor oil and castor biodiesel experiment, respectively. For the castor oil and castor biodiesel, though there was a deviation from the baseline, we cannot see at 30–65 °C an obvious endothermic and exothermic peak as that of castor oil and castor biodiesel experiment, and then 65 °C cooled to –30 °C also has no exothermic peaks for exhibiting a significant crystallization reaction. Fig. 5 shows DSC non-isothermal tests of the scanning rate selected for the programmed temperature ramp were 4, 6, and 8 °C/min for the range of temperature rise chosen from 30–300 °C for each and phase behavior experiment, respectively. From Figs. 6 and 7, there is a peak maximum temperature of ca. 190 °C and 187 °C for the exothermic reaction of castor oil and castor biodiesel, respectively. The detailed results of DSC analysis are listed in Table 1.

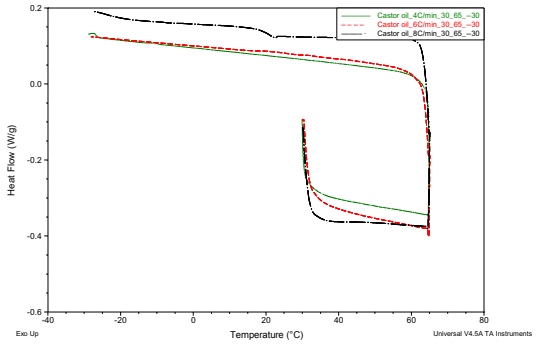

Fig. 3. DSC thermal curves of heat flow versus temperature for the dwarf-castor oil of the range of temperature rise chosen from 30–65 °C and then cooling down to –30 °C with scanning rate 4, 6, and 8 °C/min.

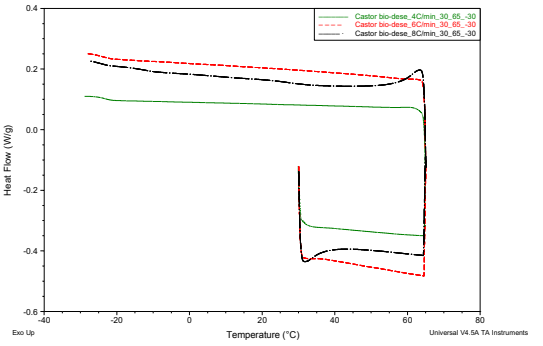

Fig. 4. DSC thermal curves of heat flow versus temperature for the dwarf-castor biodiesel of the range of temperature rise chosen from 30–65 °C and then cooling down to –30 °C with scanning rate 2, 4, 6, and 8 °C/min.

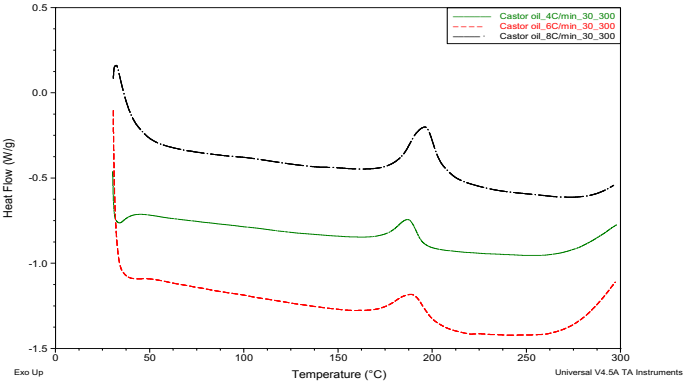

Fig. 5. DSC thermal curves of dwarf-castor oil of the range of temperature rise chosen from 30–300 °C at various with scanning rates of 4, 6, and 8 °C/min.

Table 1.Results of DSC tests of castor oil and biodiesel of the range of temperature rise chosen from 30–300 °Cat various with scanning rates of 4, 6, and 8 °C/min.

Sample	Mass[a]	Condition[b]	$ExoT_o$[c]	$ExoT_p$[d]	$Exo\Delta H$[e]
Castor oil	2.4	4	175.92	187.98	28.64
	2.5	6	171.60	190.12	37.44
	2.5	8	181.14	196.71	42.45
Biodiesel	2.0	4	147.00	171.35	37.68
	1.9	6	164.38	183.57	31.45
	1.8	8	170.29	192.47	16.23

3.3. Kinematic viscosity measurement

From Fig.6, we obtained the B100 (100% castor biodiesel) and B50 of kinematic viscosity average values of 46.50 and 12.48, respectively. Generally, the biodiesel is to be as fuel for diesel engine, the kinematic viscosity range followed the ASTM D6751 and EN 14214 specification standards, from 1.9 to 6and from 3.5 to 5.0 mm^2/s, respectively [22, 23]. It is too sticky for B100, B50, and B30 as an environmentally-friendly diesel. Meanwhile, from Fig 6, we observed B2–B20, which value of kinematic viscosity is included in a suitable range, which also shows that the high mixing ratio of environmentally-friendly diesel is B20 in this study.

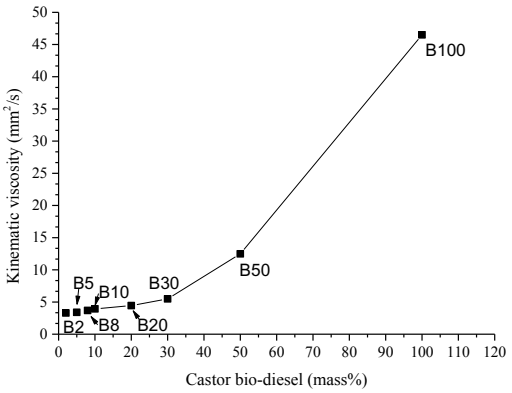

Fig. 6. Kinematic viscosity of various proportion of biodiesel for mixing with petrodiesel.

3.4. Heat of combustion measurement

In this study, for the heat of combustion of environmentally-friendly diesel, the basic value is a commercial diesel, which value was as a comparison benchmark for other diesels. From Table 2, we obtained the heat of combustion that B100, B50, and B30are less than the others, which also showed them unsuitable for an environmentally-friendly diesel. Comparisons of all samples of heat of combustion, from which could be acquired the mixed ratio of environmentally-friendly diesel smaller than B20, the fuel suitable for use in compression ignition diesel engines in this study. Meanwhile, from Table 2, we observed the B2–B20, which value of heat of combustion is included in the suitable range, which also shows the highly mixed ratio of environmentally-friendly diesel is B20 in this study.

From the above transesterified results of fatty acid via DSC tests and FT-IR spectrogram we repeatedly corroborated the accuracy of the transesterification and the specific characteristics, proving that dwarf-castor oil forms biodiesel, and then by bomb calorimeter and viscometer, we compared with the heat of combustion and the

kinematic viscosity of the various proportion of biodiesel for mixing with petro diesel, respectively, which could be used to obtain the best condition of the mixture B20 as a use suitable environmentally-friendly diesel.

Table 2. Results of heat of combustion measurements of the castor biodiesel, a commercial diesel and a commercial environmentally-friendly diesel, and the various proportion of biodiesel for mixing with petrodiesel.

Sample	Mass[a]	Δt^b	$H_b{}^c$
Diesel	0.5089	2.218	43465.074
E-diesel	0.5127	2.236	43495.774
Castor oil	0.5258	1.942	36792.449
B2	0.5170	2.328	44922.353
B5	0.5103	2.288	44724.450
B8	0.5055	2.244	44274.355
B10	0.5048	2.250	44455.000
B20	0.5073	2.210	43443.727
B30	0.5059	2.179	42947.923
B50	0.5220	2.181	41661.762
B100	0.5043	1.879	37105.483

[a]Mass: sample mass (g). [b]Temperature differences of from firing temperature to change has become constant(°C). [c]Heat of combustion(J/g).

4. Conclusions

Overall, dwarf-castor oil can be developed for biodiesel production and successfully made into suitable environmentally-friendly diesel; we have obtained the best condition of mixtures and the highly mixed rate of B20 (heat of combustion 43443.727 J/g; kinematic viscosity 4.44 mm^2/s) as an appropriate environmentally-friendly diesel of dwarf-castor's biodiesel.

Acknowledgements

The authors are grateful to National Defense University of Taiwan. We are indebted to the donors of National Science Council (NSC), Taiwan under the contract No.: NSC 102-2221-E-468-001-MY2 for financial support. In addition, we are grateful to Prof. Tzu-Wan Ho and Chang-Pin Chang for technical support on the transesterification experiments.

References

[1] H.Mutlu, M.A.R.Meier, Castor oil as a renewable resource for the chemical industry, Eur. J. Lipid Sci. Technol.112(1)(2010)10–30.
[2] R.Phillips, R.Martyn, Annuals and Biennials, London: Macmillan, 1999, p.106: ISBN 0-333-74889-1.
[3] F.A.Lateef, O.D.Onukwuli, U.C.Okoro, P.M.Ejikeme, P. Jere, Some physical properties and oxidative stability of biodiesel produced from oil seed crops, Korean J. Chem. Eng.31(5)(2014) 725–731.
[4] J.Wang, L.Cao, S.Han, Effect of polymeric cold flow improvers on flow properties of biodiesel from waste cooking oil, Fuel, 117 (2014) 876–881.
[5] P.Sivakumar, K.Anbarasu, S.Renganathan, Biodiesel production by alkali catalyzed transesterification of dairy waste scum, Fuel, 90 (2011) 147–151.
[6] S.U.Lee, K.Jung, G.W.Park, C.Seo, Y.K. Hong, W.H.Hong, H.N.Chang, Bioprocessing aspects of fuels and chemicals from biomass, Korean J. Chem. Eng. 29(7)(2012) 831–850.
[7] A.Hayyan, M.A.Hashim, M.E.Mirghani, M.Hayyan, I.M.AlNashef, Esterification of sludge palm oil using trifluoromethane sulfonic acid for preparation of biodiesel fuel, Korean J. Chem. Eng.30(6)(20130 1229–1234.
[8] S.K.Hoekman, A.Broch, C.Robbins, E.Ceniceros, M.Natarajan, Review of biodiesel composition, properties, and specifications, Renew. Sust. Energ. Rev.16 (2012) 143–169.

[9] C.G.Tsanaktsidis, S.G.Christidis, E.P.Favvas, A novel method for improving the physicochemical properties of diesel and jet fuel using polyaspartate polymer additives, Fuel,104(2013) 155–162.
[10] J.Pullen, K.Saeed, An overview of biodiesel oxidation stability, Renew. Sust. Energ. Rev.16 (2012) 5924–5950.
[11] S. Jain,M.P.Sharma, Application of thermogravimetric analysis for thermal stability of Jatropha curcas biodiesel, Fuel, 93 (2012) 252–257.
[12] R.O.Dunn, Crystallization behavior of fatty acid methyl esters, J. Am. Oil Chem. Soc.85(2008) 961–972.
[13] M.Garcia-Perez, T.T.Adams, J.W.Goodrum, K.C.,Das, D.P.Geller, DSC studies to evaluate the impact of bio-oil on cold flow properties and oxidation stability of biodiesel, Bioresour. Technol.101(2010) 6219–6224.
[14] C.P.Lin, Y.M.Chang, J.M.Tseng, C.M.Shu, Comparisons of nth order kinetic algorithms and kinetic model simulation on HMX by DSC tests, J. Therm. Anal. Calorim. 100(2)(2010) 607–614.
[15] C.P.Lin, J.M.Tseng, Y.M.Chang, S.H.Liu, C.M.Shu, Modeling liquid thermal explosion reactor containing tert–butyl peroxybenzoate, J. Therm. Anal. Calorim.102 (2010) 587–595.
[16] J.M.Tseng, C.P.Lin, Prediction of incompatible reaction of dibenzoyl peroxide by isothermal calorimetry analysis and green thermal analysis technology. J Therm Anal Calorim.107 (2012) 927–933.
[17] J.M.Tseng, T.F. Hsieh, Y.M.Chang, Y.C.Yang, L.Y.Chen, C.P.Lin, Prediction of thermal hazard of liquid organic peroxides by non-isothermal and isothermal kinetic model of DSC tests, J. Therm. Anal. Calorim. 109 (2012) 1095–1103.
[18] X.Zhang, L.Li, H.Xie, Z.Liang, J.Su, G.Liu, B.Li, Effect of temperature on the crystalline form and fat crystal network of two model palm oil-based shortenings during storage, Food Bioprocess Technol.7(2014) 887–900.
[19] Y.B.Che Man, G.Setiowaty, F.R. van de Voort,Determination of iodine value of palm oil by fourier transform infrared spectroscopy, J. Am. Oil Chem. Soc.76(6)(1999) 693–699.
[20] Y. Sun,P.Dailey, S.Deng, Optimization of biodiesel production from palm oil under supercritical ethanol conditions using hexane as co-solvent: A response surface methodology approach, Fuel, 107(2013) 633–640.
[21] S. K.Hoekmana, A.Brocha, C.Robbinsa, E.Cenicerosa, M.Natarajanb, Review of biodiesel composition, properties, and specifications. Renew. Sust. Energ. Rev.16(2012) 143–169.
[22] T.Muppaneni, H.K.Reddy, S.Ponnusamy, P.D.Patil, J.Abraham, V.R.Saravanakumar, V.V.Kulkarni, K.Sivakumar, A.P.Singh, P. Visha, Yield and quality characteristics of rendered chicken oil for biodiesel production, J. Am. Oil Chem. Soc.91(2014) 133–141.